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Short communication

Porous silica ceramics with relatively high strength and novel bi-modal pore structure prepared by a TBA-based gel-casting method

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Abstract

Porous silica ceramics with relatively high strength and novel bi-modal pore structure can be successfully fabricated via a facile *tert*-butyl alcohol-based gel-casting process by use of silica extracted from coal fly ash. Based on the evaporating of *tert*-butyl alcohol (TBA) during the drying process, the microstructure with bi-modal pores was obtained. By setting the solid loading (15 wt.%) and changing the sintering temperature from 1050 to 1150 °C, the porosity of the porous silica ceramics varied within the range of 70.1% and 72.4%, as the bulk density varied from 0.59 to 0.67 g/cm^3 and small pore sizes from 3.31 to 2.89 nm. The compressive strength of sintered silica ceramics increased from 4.38 MPa to 5.82 MPa, which was attributed to the 3D-framework structure and the connection of silica particles.

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Keywords: D. SiO$_2$; Microstructure; TBA-based gel-casting

1. Introduction

Porous ceramics have received much attention for the special pore structure that endows them with a specific set of properties, such as low bulk density, low specific heat, low thermal conductivity, high surface area, and high permeability [1–3]. These properties are expected to make them promising candidates for a variety of technological applications, such as catalyst carriers, thermal insulation and so on [4]. Porous silica has been proven to be a very promising material due to its low density, good thermal and mechanical stability, super paramagnetic and chemical inertia [5–7]. Nowadays, silica aerogels have been studied extensively because of their unique properties, such as low density ($\sim$0.03 g/cm^3), high porosity ($\sim$99%), low thermal conductivity ($\sim$0.02 W/mK) and high surface area ($\sim$1000m^2/g) [8,9]. However, the usual route for the production of silica aerogels includes supercritical drying and the use of raw materials, such as tetraethylorthosilicate (TEOS), which are obstacles to commercialization due to their prohibitive expense [10]. Besides, it's hard to expand their engineering applications because of the ultra low mechanical strength. In this work, although the porosity of porous silica ceramics is much lower than the silica aerogels, the unique network structures make it possible for them to obtain higher mechanical strength, which make them easy to handle during the fabrication process and more adaptive to the working condition. There is no experimental data in the literature for the preparation of nano-porous silica ceramics with novel bi-modal pore structure by use of silica extracted from coal fly ash and this method.

The objective of the present work is to facilitate the recycling of coal fly ash and to produce nano-porous silica ceramics by *tert*-butyl alcohol-based gel-casting process. This novel gel-casting technique induced pores by the evaporation of solvent, without using any pore-forming agents. In this paper, nano-porous silica ceramics with relatively high strength and novel bi-modal pore microstructure were successfully fabricated. By setting the solid loading (15 wt.%), the properties and pore size distribution of porous silica ceramics were investigated with the increasing of sintering temperature.

2. Experimental procedure

2.1. Raw materials

In this work, nano silica particles (about 50 nm) were extracted directly from coal fly ash (Shanxi Province, China) by

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Table 1
Chemical composition of the as-received silica powder in this work.

Component (wt.%)					
SiO_2	$A1_2O_3$	Na_2O	Fe_2O_3	TiO_2	Others
98.51	0.757	0.3419	0.228	0.0247	0.1384

alkali leaching, which was reported in another paper [11]. The chemical compositions of as-received silica powder are shown in Table 1. *tert*-butyl alcohol (TBA, AR grade) was used as shaping solvent and pore forming agent in gel-casting process. A premix solution of monomer and cross linker was prepared in TBA with acrylamide (AM, $C_2H_3CONH_2$) and N,N′-methylenebisacrylamide (MBAM, $(C_2H_3CONH)_2CH_2$) the weight ratio is AM:MBAM:TBA = 20:2:100. Ammonium per sulfate (APS) and N,N,N′,N′-tetramethylethylenediamine (TEMED) are used as initiator and catalyst for gelation reaction, respectively. To produce stable silica suspensions in liquid TBA, citric acid was used as dispersant (2 g per 100 g slurry). All chemicals used in this study are analytical (AR) grade.

2.2. Fabrication procedure

A slurry mixture including silica powder, TBA, AM monomer, MBAM cross linker and citric acid solution was prepared by ball milling for 4 h. The prepared slurries with 15 wt.% solid loadings were found to be stable and had good flow ability for casting. Silica suspensions were then added with initiator solutions (15 wt.% in water) and catalyst, poured into polyethylene molds. The polymerization of AM occurred in several minutes, and green bodies with high strength were obtained. After about 0.5 h, green bodies were removed from molds and dried at a temperature of 50 °C. TBA could be evaporated completely after 12 h leaving pores behind in the bodies. The dried samples were then sintered at different temperatures from 1050 to 1150 °C for 2 h, assisted by holding at 600 °C for 0.5 h to decompose the organic phase.

2.3. Characterization

The microstructures of fired specimens were observed by means of scanning electron microscopy (XL30, Philips, Netherlands). The density and open porosity of the sintered samples were measured by a conventional method using Archimedes' principle in distilled water medium. The compressive strength of cylindrical samples 12 mm in diameter and 25–30 mm in height were measured by an universal testing machine (NYL-500A) with a crosshead speed of 0.5 mm/min. Five specimens were used to determine the average value. The N_2 porosimetry was measured by a pore size distribution analyzer (NOVA 3200e).

3. Results and discussion

Fig. 1 shows the small pore forming schematic diagram in the TBA-based gel-casting process. TBA can vaporize very easily and form pores in the ceramic bodies during the drying process at 50 °C. As shown in Fig. 1(a) and (b), the AM polymerized to form a strong polyacrylamide network which was responsible for the high strength of the green body, and the pores connected with each other and distributed homogeneously throughout the green body. After sintering, as shown in Fig. 1(c), the polyacrylamide removed completely, and the silica particles lapped with each other to form the loose skeleton structure and a little shrinkage of samples occurred. It can be concluded from the schematic drawing and the SEM microstructure (Fig. 2C and D) that the most important characteristics of the porous structure were the uniformity and the interconnection of pores with sizes about 3 nm.

Fig. 2 reveals the SEM microstructure of green body with 15 wt.% solid loading after evaporating. Comparing with water, the saturated vapor pressure of TBA is higher (6.4 kPa) and the surface tension force is lower (15.15 mN/m) [11]. Therefore, the TBA can vaporize very easily and form pores in the ceramic bodies during the drying process at 50 °C. It can be concluding from Fig. 2 that there is a novel structure with two noticeable pore types: the large spherical pores and the small windows on

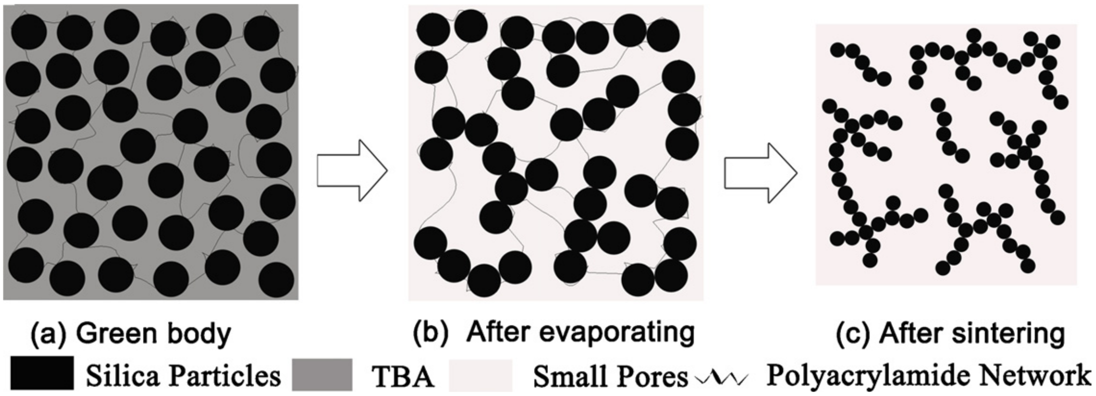
(a) Green body (b) After evaporating (c) After sintering

Fig. 1. (a–c) Schematic drawing of small pores in the porous silica ceramics prepared by TBA-based gel-casting.

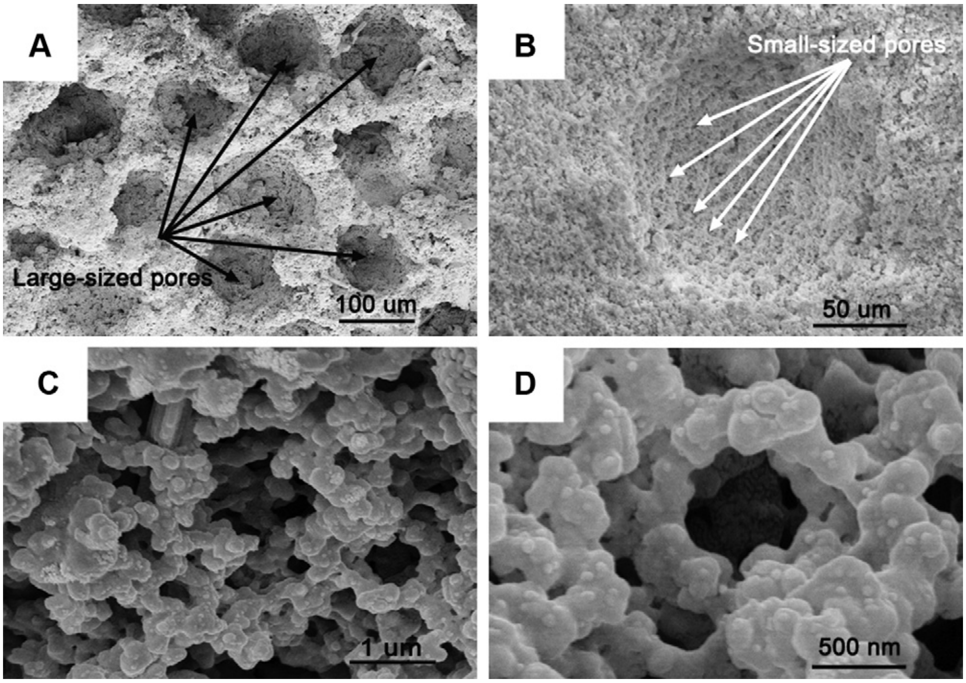

Fig. 2. SEM microstructure of green body with 15 wt.% solid loading after evaporating: (A) large-sized pores; (B) small-sized pores; (C) the structure of small pores; (D) typical connections of silica particles in green bodies.

Table 2
Properties of nano-porous silica ceramics with 15 wt.% solid loading after sintering at different temperature.

Sample	Solid loading (wt.%)	Sintering temperature (°C)	Porosity (%)	Bulk density (g/cm^3)	Compressive strength (MPa)
A	15	1050	72.4 ± 2.2	0.59 ± 0.05	4.38 ± 0.15
B	15	1100	71.4 ± 2.0	0.63 ± 0.04	5.05 ± 0.25
C	15	1150	70.1 ± 2.3	0.67 ± 0.06	5.82 ± 0.18

the walls of spherical pores. This novel structure and the interconnection of small-sized pores are the most important structure characteristics of nano-porous silica ceramics prepared in this work. The pores connected with each other and distributed homogeneously. AM polymerized to form a strong polyacrylamide network, After sintering, the polyacrylamide removed completely, the silica particles lapped with each other to form the loose skeleton structure.

Table 2 shows the properties of nano-porous silica ceramics with 15 wt.% solid loading after sintering at different temperature. Due to the process of sintering densification, the porosity of porous silica ceramics decreased from 72.4 to 70.1% and the bulk density increased from 0.59 to 0.67 g/cm^3, when the sintering temperature increased from 1050 to 1150 °C. Fig. 2D shows the typical connection of particles from which the structure similar to stone arch bridges. These unique 3D-framework structures made it possible for the bodies to obtain relatively high mechanical strength, easy to handle during the fabrication process. The compressive strength increased from 4.38 MPa to 5.82 MPa with the increasing of sintering temperature from 1050 to 1150 °C. Because raw nano silica particles were extracted directly from coal fly ash by alkali leaching, there were some other oxides in the compositions, such as Na_2O and CaO, which accelerated the sintering and densification of silica compacts.

Fig. 3 shows the details of pore morphology and interconnection of small-sized pores in the porous silica ceramics with 15 wt.% solid loading after sintering at 1150 °C. A bi-modal hierarchical structure is composed by large-sized pores larger than 50 μm and small-sized pores in walls. The boiling temperature of TBA is 82.4 °C, which is much higher than 50 °C. So the reason for the presence of these spherical large pores was the possibility of entrapped air during mixing, and the small-sized pore structure was a consequence of the pore formation during the experimental process: TBA volatilized at 50 °C for 12 h, and PMA was burned out when the temperature reached approximately 600 °C. Fig. 3D shows the typical 3D-framework of small-sized pores from which the structure similar to stone arch bridges and the sintering neck can be easily observed. The interconnected pores were homogeneously dispersed in the silica matrix and adjacent particles interconnected to form a strong skeleton.

Fig. 4 shows the pore size distribution of green body and porous silica ceramics sintered at different temperature. As being sintered, the small pores (1.85 nm) in green body disappeared and combined to form large pores (3.31 nm). Each sintered sample presented a single peak with narrow half-peak

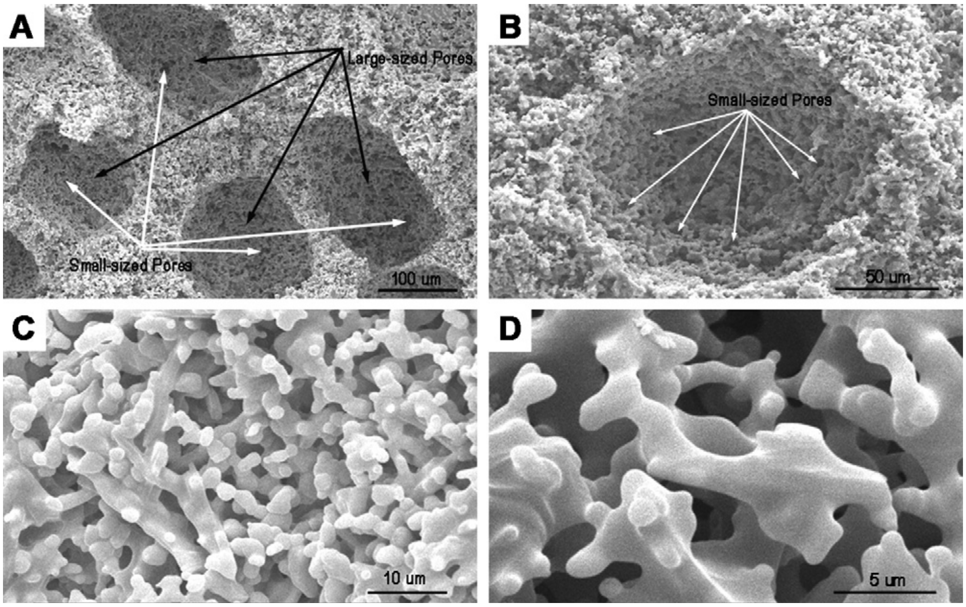

Fig. 3. SEM microstructure of green body with 15 wt.% solid loading after sintering at 1150 °C: (A) large-sized pores; (B) small-sized pores; (C) the structure of small pores; (D) typical 3D-framework.

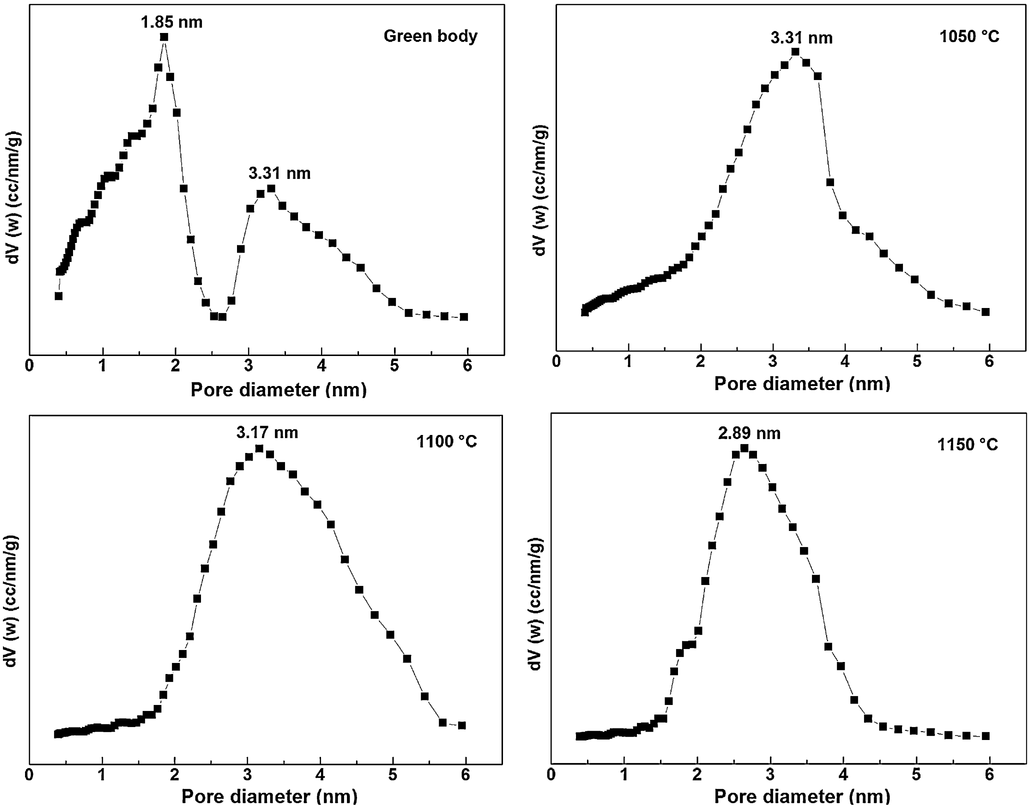

Fig. 4. Pore size distribution of green body and samples sintered at different temperature.

width, signifying a uniform pore size distribution. It can be concluded that with a given initial solid loading (15 wt.%), the sintering temperature significantly contributes to the change of porosity and pore size. As the sintering temperature increased from 1050 to 1150 °C, the pore size of samples decreased from 3.31 to 2.89 nm.

4. Conclusion

A novel *tert*-butyl alcohol-based gel-casting was developed to prepare nano-porous silica ceramics with hierarchical bi-modal pore structure by use of silica extracted from coal fly ash. The solid loading of slurry in this gel-casting process was much lower than conventional water-based gel-casting, so highly porous silica ceramics with low density were obtained. By setting the solid loading (15 wt.%) and changing the sintering temperature from 1050 to 1150 °C, the porosity of the porous silica ceramics varied within the range of 70.1% and 72.4%, as the bulk density varied from 0.59 to 0.67 g/cm^3 and small pore sizes from 3.31 to 2.89 nm. As being sintered, the small pores (1.85 nm) in green body disappeared and combined to form large pores (3.31 nm). The compressive strength of sintered silica ceramics increased from 4.38 MPa to 5.82 MPa, which was attributed to the 3D-framework structure and the connection of silica particles.

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